SOME OPTICAL SPECTRA STUDIES OF THE RARE EARTH ATOM SAMARIUM IN INERT GAS MATRICES AT 4.2°K.

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ABSTRACT

The optical spectrum of samarium atoms trapped in matrices of argon and krypton at 4.2°K was examined. A simple basis for interpretation of the results is presented, in which the matrix perturbation is applied to the free atom in some quantum state of total angular momentum J.

The spectra can be correlated with the published data for SmI, but the complexity of the results, particularly in argon, make a detailed interpretation difficult. Some exceptionally sharp triplets with small splittings are considered to be derived from levels of the excited $4f^5 5d 6s^2$ configuration, none of which has previously been identified. Fluorescence was observed, corresponding to transitions from an excited state to the $^7F_1$ and $^7F_2$ levels of the ground state.

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Some Optical Spectra Studies of the Rare Earth Atom Samarium in Inert Gas Matrices at 4.2°K.

Introduction

The comparatively recent experimental technique for trapping free radicals (1) is a useful tool in the study of these reactive species. In this laboratory, the most favored form of this technique consists in diluting the radicals with an inert gas stream and allowing the resulting mixture to impinge on a cooled surface. Usually, the coolant is liquid helium, at 4.2°K. The radicals are present in such low concentration that each one is completely isolated in a matrix of inert gas atoms.

Subsequent spectral studies of the deposit are considerably simplified, due to the low temperature of the species, since only transitions from the ground state energy level are generally involved.

In all but the most superficial investigations, the weak interactions between the trapped species and its environment must be considered in interpreting the results. Indeed, the strong interest in these fundamental interactions has resulted in studies of simpler systems, using the same experimental technique. A useful empirical treatment was presented by Robinson and McCarty (2) who examined the spectra of sodium and mercury atoms in inert gas matrices. Their results showed that the transition energies for the atoms were only slightly affected; in addition, the orbital degeneracy for the excited P state was completely removed since three lines were seen. The problem of spectral shifts in matrices was also treated in a recent theoretical paper by Coulson and Jortner (3).

Readily vaporized metals were chosen for study; in each case, the free atom spectrum consisted effectively of a single isolated line in the region of interest. The electron configuration of the atoms was relatively simple, consisting of a series of completely filled shells, the outermost one being an s shell. In the spectral transitions of interest, an outer s electron is promoted to a p orbital of the same shell, or the next higher one. Since the trapped atom is closely surrounded by the inert gas atoms, such transitions are significantly perturbed, and splittings of the order of 10^2 cm^{-1} are observed. All the lines are broad.

This work arose from the suggestion that a rare-earth atom, with a configuration involving a partially-filled inner 4f sub shell (Table 1) and a more complex system of energy levels would be an interesting subject for investigation using this technique.

Transitions involving a rearrangement of only these 4f electrons might be seen, as in the spectra of crystals of rare-earth salts (4). In interpreting the latter spectra, crystal field theory is a valuable tool, the field being considered as a perturbation on the ion in some quantum state of total angular momentum J. Standard crystal field theory considers only first-order contributions to the degeneracy splitting, and treats the perturbation Hamiltonian as a sum of one-electron terms. It follows that only those interactions with electrons in partially-filled shells contribute to the splittings. Some analogous deductions which follow when the theory is cautiously applied to this trapped atom case are quite reasonable. The splittings for f-f transitions in crystals of rare-earth salts is small (10-100 cm^{-1}). In these crystals, interaction between the 4f electrons, with three outer shielding electrons removed, and the surrounding ions of the

Table 1

Symbol	Atomic Number	Configuration of Neutral Atom	Ground State	*Boiling Point °K
La	57	$5d6s^2$	$^3D_{3/2}$	3742
Ce	58	$4f^26s^2$	(^3H)	3741
Pr	59	$4f^36s^2$	^4I	3400
Nd	60	$4f^46s^2$	$^5I_4$	3300
Pm	61	$4f^56s^2$	(^6H)	-
Sm	62	$4f^66s^2$	$^7F_0$	2173
Eu	63	$4f^76s^2$	$^8S^0_{7/2}$	1712
Gd	64	$4f^75d6s^2$	$^9D^0_2$	3273
Tb	65	$4f^85d6s^2$	(^8H)	3073
Dy	66	$4f^{10}6s^2$	(^5I)	2873
Ho	67	$4f^{11}6s^2$	(^4I)	2873
Er	68	$4f^{12}6s^2$	(^3H)	3173
Tm	69	$4f^{13}6s^2$	$^2F^0_{7/2}$	2000
Yb	70	$4f^{14}6s^2$	$^1S_0$	1700

Values in parentheses are uncertain

* Reference 14

crystal field is much stronger than in the case of the neutral atom surrounded by inert gas atoms. Consequently, there was some interest in discovering whether these transitions would be accompanied by observable splittings; the lines were expected to be quite sharp, since the perturbation is slight. Such transitions are of course forbidden in the free atom for the important case of electric-dipole radiation, but would be weakly allowed for the trapped atom if its environment lacked a center of symmetry. Allowed outer electron transitions as in the case of the simpler atoms would of course be seen. Thus the rare earth atom spectra were expected to show the usual broad lines with wide splitting, and possibly some very sharp lines with small splittings, corresponding to forbidden f-f transitions.

Since the experimental procedure required the metal to be vaporized, apparently only the readily volatile metals had hitherto been studied. Hence, a simple solution to the attendant vaporization problem for the comparatively high melting rare-earth metals would be a useful practical extension of the technique.

The particular rare earth to be used was chosen on the basis of its availability, volatility, and spectral data. Naturally, the atom was required to show absorption in the accessible region, preferably in the visible. The review by El'yashevich (6) is the most recent and comprehensive source for the spectra of the rare earths. At present, the only typical rare-earth metals whose neutral free atom spectra have been characterized to any significant extent are samarium, europium, and gadolinium. The gadolinium spectrum is especially complex since the ground state configuration includes a 5d electron (Table 1). Europium has the simplest spectrum, due to the fact that its 4f shell is exactly half-filled. (The following brief comments anticipate the final discussion, where their basis is presented.) However, with a ground state $^8S^o_{7/2}$, excited states of europium would have J = 5/2, 7/2, or 9/2 and the splitting of these highly degenerate levels was expected to be quite complex, even though the two-fold Kramers' degeneracy (7) would of course remain. Samarium has a ground state $^7F_0$, and with J = 0, this should not be split. Moreover, in transitions from this $^7F_0$ level, the excited state can have J = 1 only and so a further spectral simplification results. The metal, as its low boiling point suggests, is one of the more volatile members of the group; it was also available in high purity. Consequently, samarium was selected for study.

Experimental Procedures

The elements of the technique are illustrated schematically in Figure 1. The heart of the apparatus is the liquid helium cooled quartz cold finger, on which the incoming inert gas and metal vapor streams are condensed, this deposit being subsequently examined spectroscopically. Figure 2 shows the arrangement of Dewar vessels and pumping equipment involved in maintaining the quartz cold finger.

Some suitable method for vaporizing the samarium metal was needed. Unfortunately, space restrictions dictated by the cold finger environment made the problem more than a trivial one. Thus, the vaporizer could take up no more space than that of a cube of about 3/4" side, and temperatures well in excess of 1000°C were required of it.

The samarium metal, obtained from Research Chemicals Inc., Burbank, was 99.7% pure, with oxygen and tantalum as principal impurities. It was available only in irregularly shaped pieces, but fortunately these

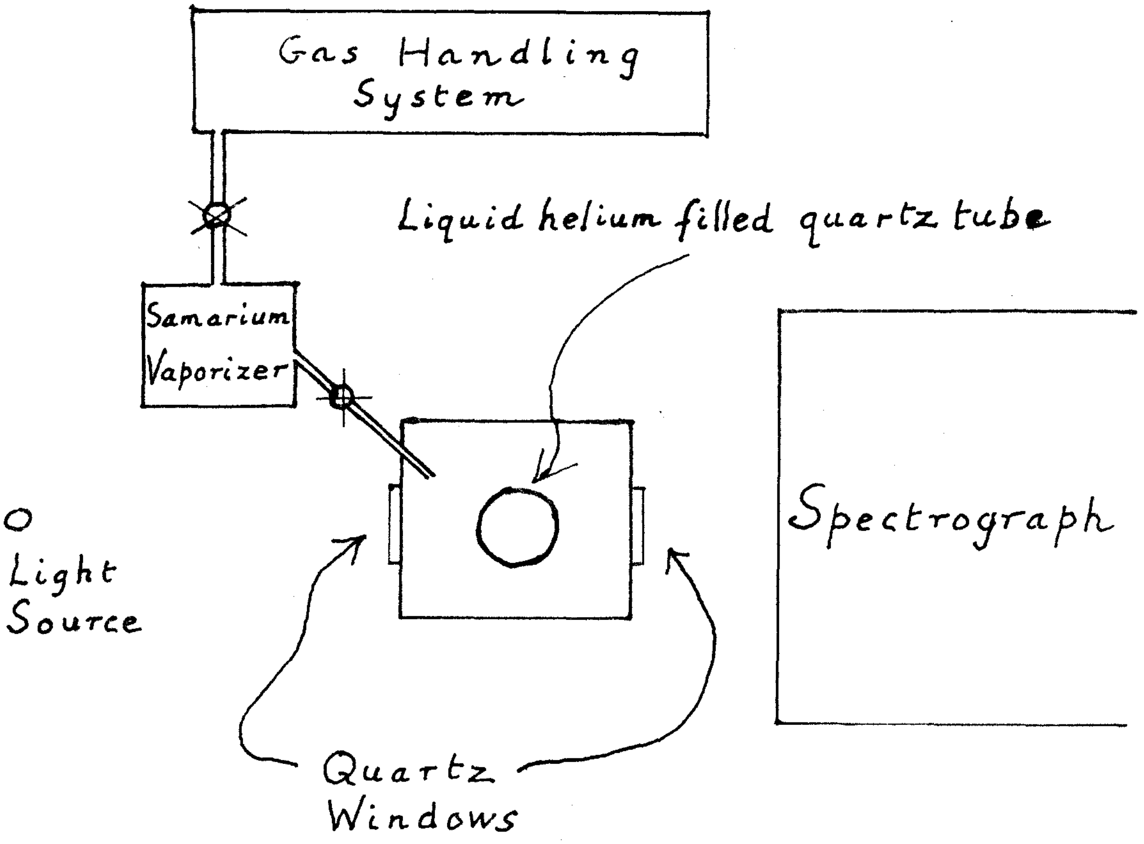


Fig. 1

Simplified schematic representation of experimental set-up.

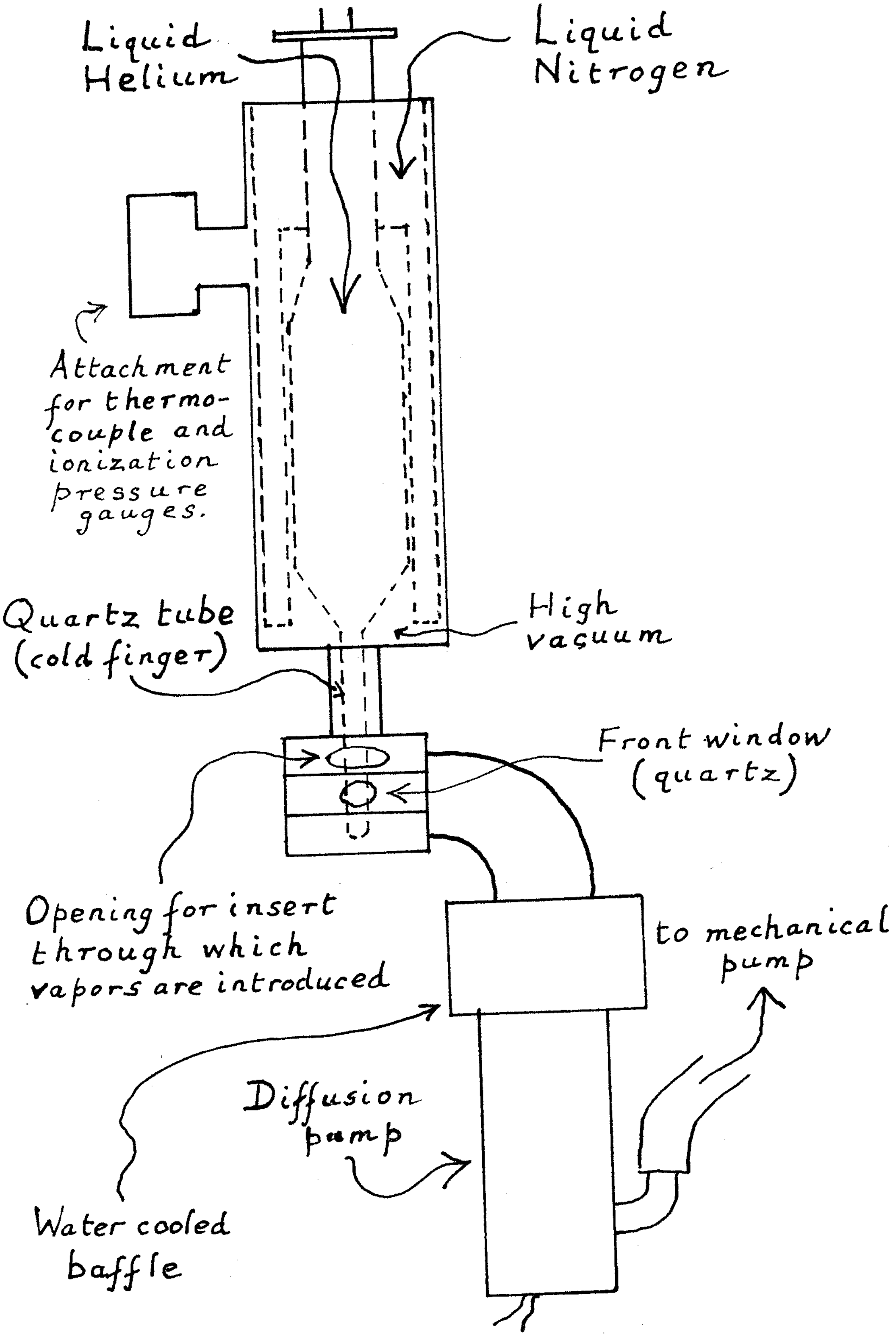


Fig. 2

Cold finger system (metal construction).

could be cut with a sharp steel edge; traces of iron impurity may have been introduced by such treatment. The metal was stored under hexane.

Various electrically heated tantalum boats were fabricated and tested, but they were either too weak mechanically, or required prohibitively high currents, not readily handled by available equipment. In another approach, the metal was readily vaporized by striking an arc between two electrodes tipped with samarium, but the method was difficult to control. Finally, a simple readily controlled vaporizer was made by spot-welding a small piece of samarium metal to a tungsten wire through which current could be passed. Currents up to about 30 amps were adequate and these were readily available from D.C. outlets. Figure 3 shows the details of the vaporizer in its final form, together with the insert into the cold finger system. This insert, incorporating the inlet tube for the inert gas stream, was permanently attached to the cold finger and gas handling systems throughout this series of experiments, but the vaporizer was of course removable.

Preparation of Samarium Metal prior to Run

In a procedure for checking and cleaning the metal

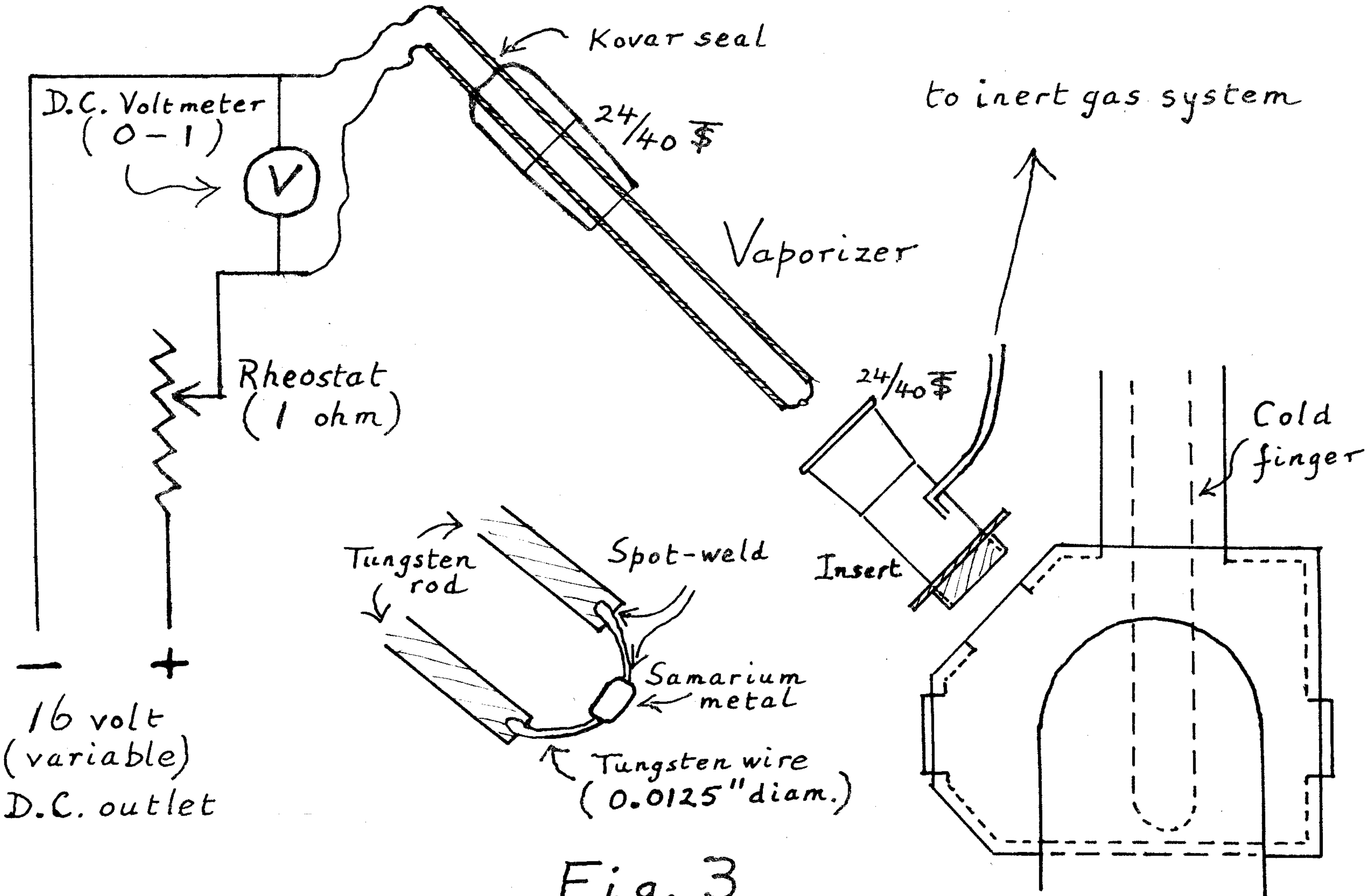


Fig. 3
Vaporizer, insert, and section of cold finger system prior to assembly. An enlarged detail of the vaporizer is also shown.

vaporizer before insertion into the cold finger system, the samarium was heated in a stream of hydrogen gas. An interesting green-blue glow was observed around the samarium when it was heated in a hydrogen discharge, probably due to emission from excited samarium atoms in the vapor. In later runs, the metal was cleaned by carefully filing the surface.

Procedure during a Run

The lining up and adjustment of the spectrograph and optical system, once accomplished, required no attention in subsequent experiments. Between runs, the inert gas system (Figure 4) was isolated by closing stopcock C, while a pressure of about 4×10^{-4} mm or less was usually maintained continuously in the cold finger system by the mechanical pump. Before an experiment, this pressure was checked and the diffusion pump turned on, with a properly adjusted rate of cooling water. A high flow rate of cold water was continuously passed through the baffle above the diffusion pump. While this part of the apparatus was pumping down, the inert gas system was pumped out, the trap D being cooled with liquid nitrogen. After attaining a pressure of a few microns, the gauge on the inert gas tank was checked

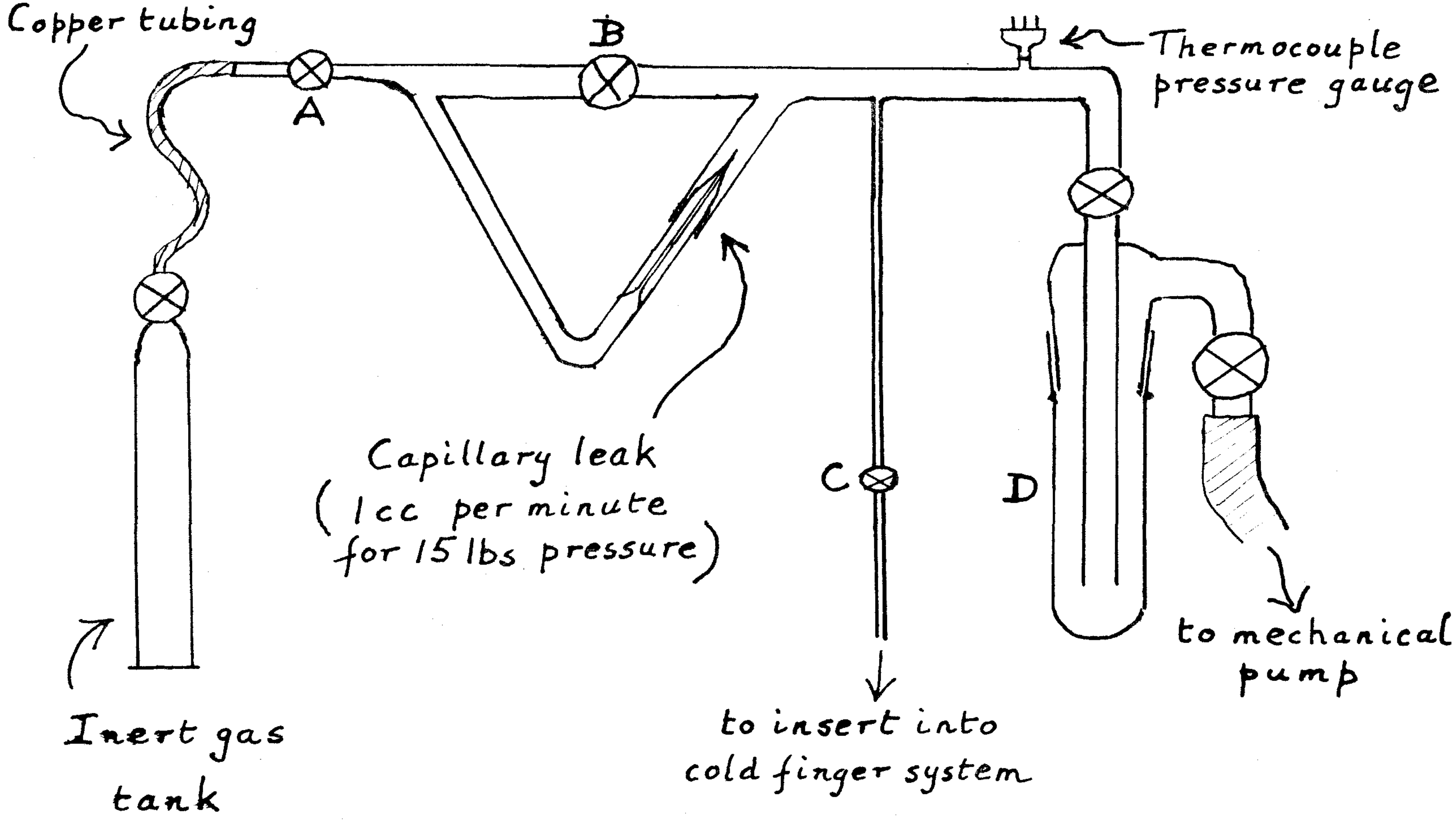


Fig. 4
Inert gas system.

for leaks by closing stopcock A, opening the tank only to the gauge, keeping the delivery valve closed, then closing the tank and checking for any drop in the gauge pressure reading over the next few minutes. In the meantime, any water in the nitrogen Dewar over the cold finger was removed by use of an aspirator line, rinsing out the Dewar two or three times with a little methyl alcohol.

The diffusion pump reduced the pressure around the cold finger to about 5×10^{-5} mm. Addition of liquid nitrogen to the Dewar brought this down further to 2×10^{-6} mm. This outer Dewar was kept filled throughout the run. Subsequently, the inner Dewar was filled with liquid helium according to a standard procedure (1), and all was ready for the deposition process.

With a delivery pressure of about 2 lbs. from the inert gas tank, stopcock A was opened. B was closed, and C opened when the thermocouple pressure gauge read 200 microns, the steady pressure in the inert gas system whenever deposition was taking place. The vaporization of the samarium metal was begun immediately, using a voltage usually of about 0.29 across the vaporizer, and a D.C. source of 16 volts. These values were determined in earlier runs.

The plate holder was removed from the spectrograph and the spectrum examined visually. In this way, the deposition could be stopped immediately when evidence of the strong absorption lines in the visible first appeared. Spectra were photographed, with repeated deposition if desired, until the liquid helium was exhausted and the deposit disappeared. Finally, the vaporizer and diffusion pump were turned off and the inert gas system shut down.

Experimental Results and Discussion

Absorption spectra in the range 3700 Å-8000 Å were obtained. A grating instrument, built in this laboratory, was used, and both light and heavy deposits of samarium were examined in matrices of argon and krypton.

Before attempting an interpretation of the results, the free atom data was examined. The spectra of the rare-earth atoms are enormously complex, and still largely uncharacterized. Thus, Albertson (8), considering only the selection rule for J, the total angular momentum quantum number, estimates that there are 18,000,000 lines expected for a one electron transition in gadolinium, while adherence to the weak selection rules for L and S in addition to J reduces the number to 20,000. In contrast, the same transition in caesium gives rise to two lines.

It is found that Russell-Saunders coupling holds fairly well for the rare-earths. Albertson's partial analysis of the spectral lines for SmI (8,9) is the principal data source for this spectrum. The only subsequent work reported was a study of the effect of isotopic displacement on the lines, carried out by Brix and Kopferman (10, 11). Their results showed that in the region up to 18,000 cm^{-1}, all the levels are due to the configuration $4f^6 6s6p$, while at higher energies, levels due to other configurations, doubtless containing 5d electrons, also appear.

In the rare earths, spin-orbit interaction is considerable, while the perturbation of a trapped atom by the surrounding inert gas matrix is comparatively small. Thus, for these outer shell transitions in samarium, following Bethe's scheme in crystal field theory (12) the matrix effect may be considered as a perturbation on the free samarium atom in some particular state of total angular momentum J. This is fortunate, for as mentioned earlier, at 4.2°K only transitions from the ground state $^7F_0$ will occur, and thus all excited states should be J = 1 states. Remembering the results of the earlier studies, it was expected that the degeneracy of these upper levels would be removed by the matrix giving a series of triplets in the spectrum. The simpler regions of the spectra obtained do indeed show a triplet structure.

Accordingly, the assignments in the data on SmI (8,9) were examined, and all upper levels of the observed allowed transitions, with J = 1 were tabulated. In only three cases were the term and configuration of the level also known. An energy level diagram was plotted and compared with the data obtained for the samarium atom in krypton (Figures 5(a), 5(b), 6(a), and 6(b).) A general correlation is observed for the lines seen strongly in absorption in SmI. However, the spectra are complex and any detailed identification is difficult. Additional uncertainty results from the fact that the SmI data include some unclassified lines, while many lines were not even tabulated, being possibly spurious. In particular, the spectral data for levels above 24,000 cm^{-1} is admittedly questionable (9). The

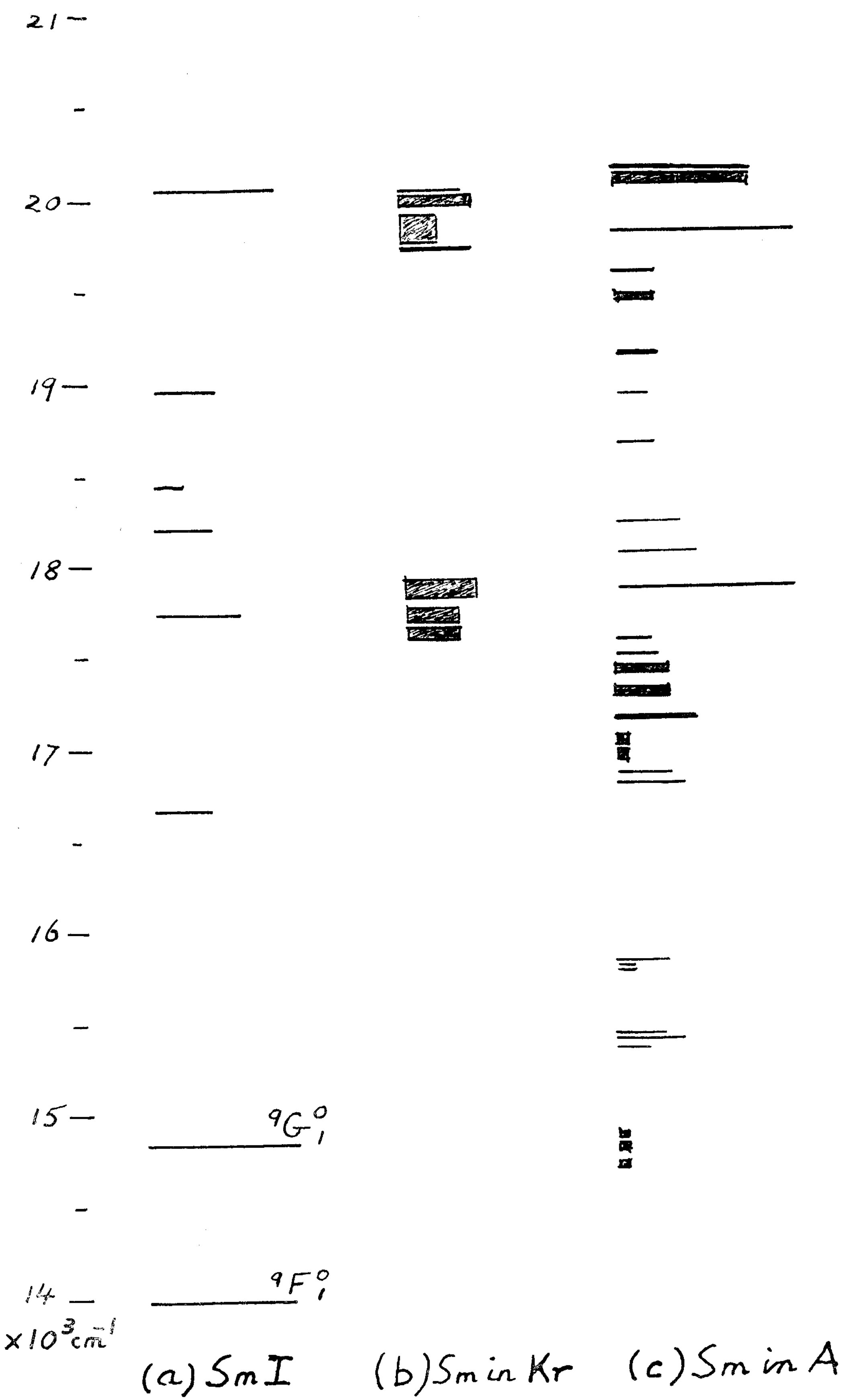
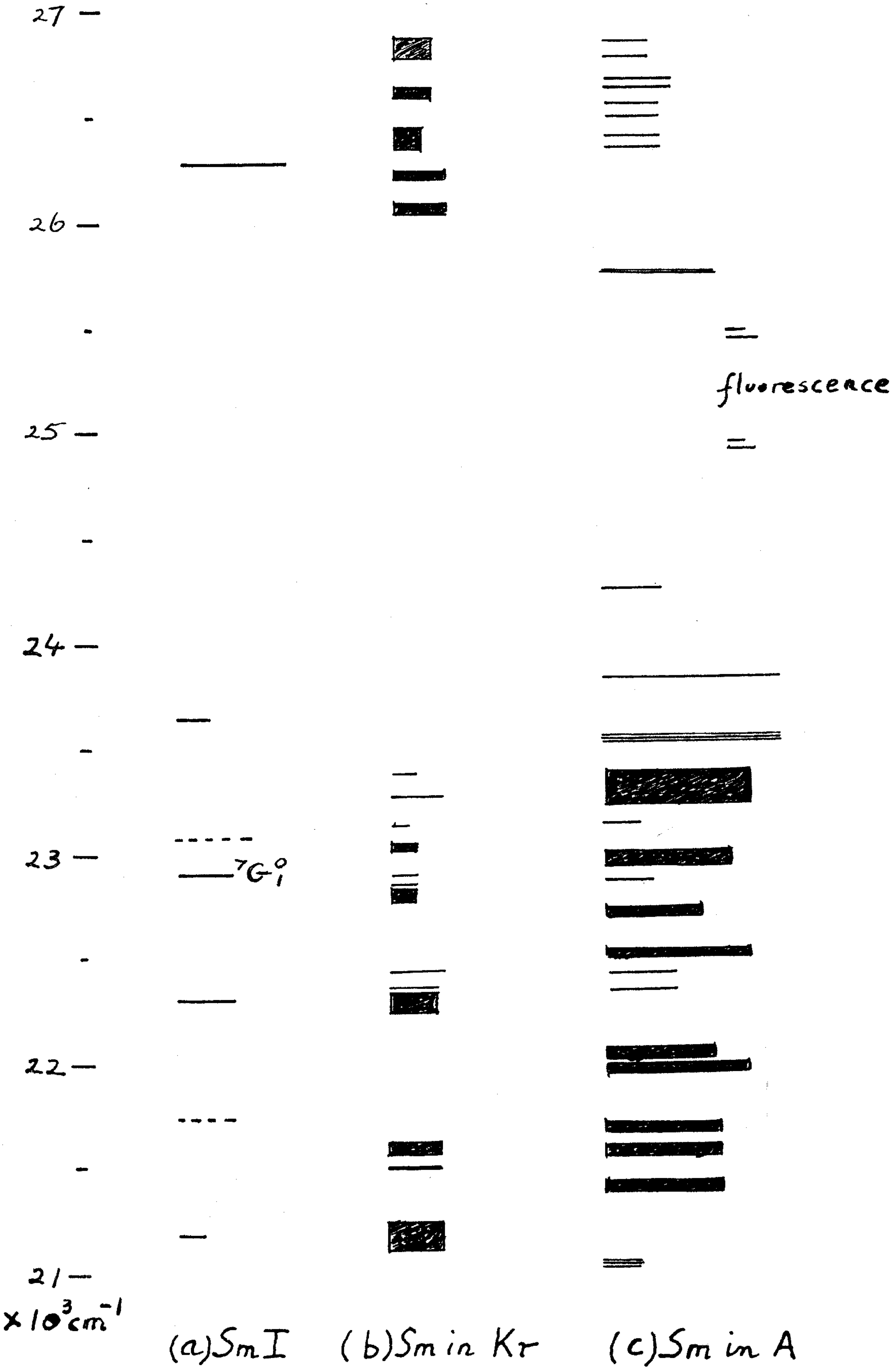


Fig. 5



Two unclassified lines ---- shown

Fig. 6

basis for interpretation, outlined above, may be oversimplified, and a more refined approach might involve the combination of the spin-orbit and matrix effects as one perturbation, with some breakdown of the J selection rule.

The two lowest levels observed strongly in SmI are not seen in krypton. They are of interest since their configuration and term origins are known; both lines derive from spin forbidden transitions from the ground state ($^7F_0 - {}^9F_1^o$ and $^7F_0 - {}^9G_1^o$) and may in fact be comparatively weak in these spectra. The spectrum in argon (Figures 5(c), 6(c)) is quite complex, showing many more lines; this may be due to a heavier samarium deposit, or there may be more than one trapping site in argon, as suggested in similar studies (2,13). Only the gross features of the spectrum in argon can be correlated with those in krypton, and in the two cases, around 18,000 cm^{-1} and 20,000 cm^{-1}, where some definite line correlation can be seen, a small shift to longer wavelengths in krypton is observed. The lines in krypton are generally broader, probably reflecting the higher polarizability of krypton over argon. All spectral data are recorded in Table 2.

As anticipated, two distinct spectral features were displayed. More commonly, the lines were fairly broad and showed wide splittings, but during the course of several studies using argon, a few distinctly sharp triplets with total splittings of about 20 cm^{-1} were observed, as follows:

(i) 21,073 21,080 21,087 cm^{-1}
(ii) 23,568 23,579 23,590 cm^{-1}
((iii) 25,880 25,900 (probably in fact a triplet))

Figure 7 shows examples of these contrasting features. At the beginning of the work it was thought that f-f transitions might be observed as very sharp lines with small splittings. However, these would be extremely weak in absorption, if allowed, while the above narrow sharp triplets are among the strongest features of the spectrum, indicating that these transitions are strongly allowed in the free atom. The two principal electronic transitions in this region for SmI are:

(a) $4f^6 6s^2 — 4f^6 6s6p$
(b) $4f^6 6s^2 — 4f^5 5d6s^2$

In transition (a) an outer 6s electron is promoted to an outer 6p orbital, and the excited state should interact strongly with the surrounding inert gas atoms to give

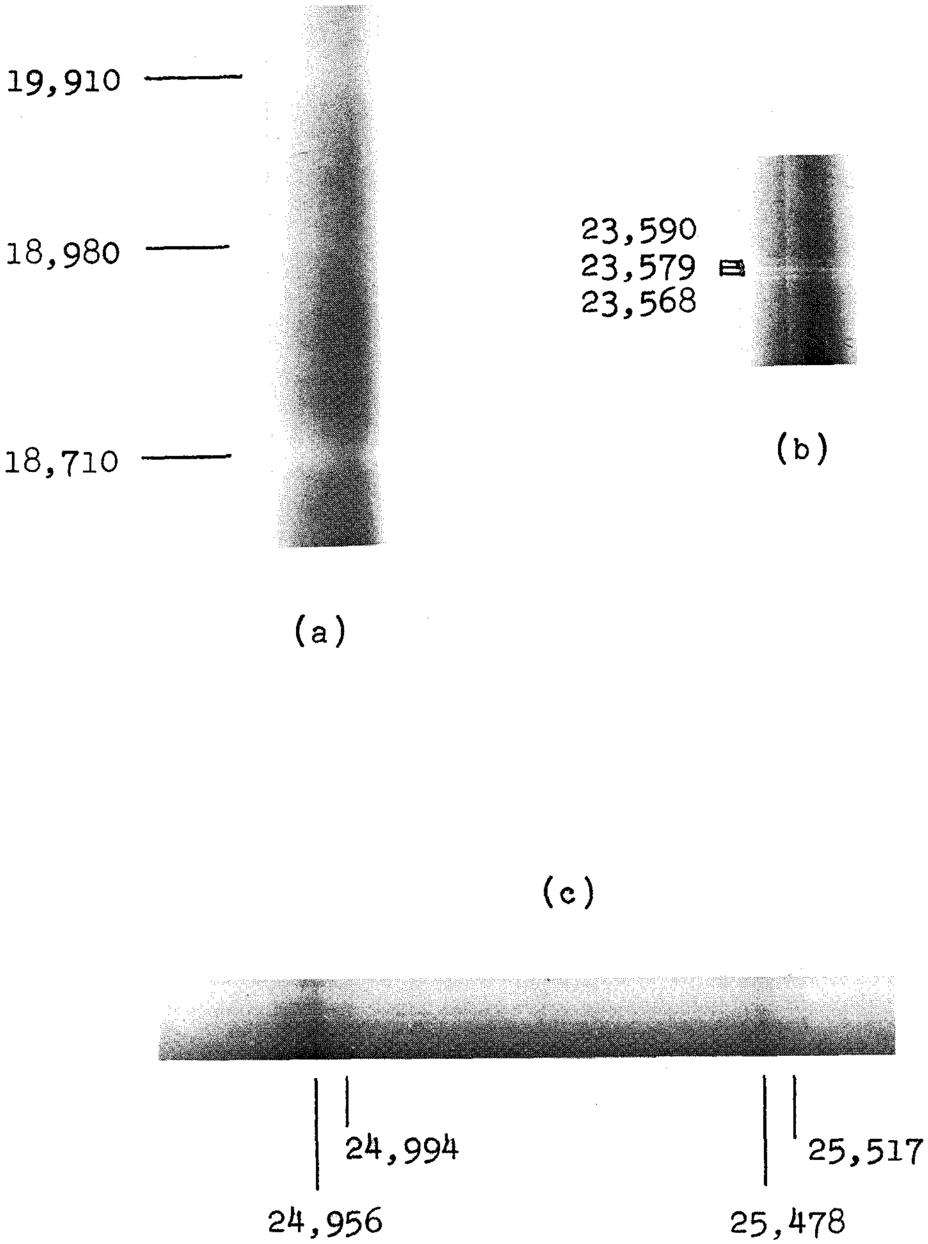


Figure 8.

Examples of { (a) usual, broad, spectral feature
(b) sharp, closely spaced triplet
(c) Fluorescence spectrum

(energies in wavenumbers)

wide splittings and broad lines. However, in transitions of type (b) only inner shell electrons are involved, and the perturbation on these electrons due to the matrix should be much smaller, resulting in sharp lines and small splittings. The observed sharp triplets must correspond to excited levels with the configuration $4f^5 5d 6s^2$. None of these levels has so far been identified in the spectrum of SmI, presumably awaiting data on the magnetic splitting of the lines. Hence, this technique may be a useful tool in further unravelling the rare earth spectra. For example, the level at 21,193 cm^{-1} in SmI (8) probably derives from the $4f^5 5d 6s^2$ configuration.

With heavier samarium deposits, these sharp triplets cannot be resolved, and appear as single broad lines. Hence, some of the lines in the spectra may in fact be such unresolved triplets. A painstaking series of experiments, with special emphasis on control of samarium atom concentration should resolve the question.

Fluorescence was also observed. In Figure 7, two distinct sets of emission lines can be seen, with separation 520 cm^{-1} corresponding to transitions to the ground state levels $^7F_1$ and $^7F_2$, which show this separation in the free atom. This affords further evidence of the close correlation between the trapped and free atom.

Some comments on the trapping site for the atom are in order. The fairly sharp reproducible spectra obtained indicate that probably only one site is involved, although in argon, which gives rise to more complex spectra, two sites may be important. Data for crystals of argon, krypton, and samarium are shown in Table 3. Foner et al (13) have discussed the three principal trapping sites for an atom in a rare gas matrix, and in the case of samarium the atomic dimensions indicate that the substitutional site, with cubic symmetry, is the only one feasible. However, the complete removal of threefold degeneracies of the atom suggests that the inert gas crystal is distorted by the trapped atom, resulting in a symmetry not exceeding orthorhombic.

Table 2

(a) SmI levels with J = 1, observed in absorption. (Two unclassified levels are included.)

(Reference 8)

Energy (cm^{-1})	Relative Absorption Intensity
13,999.53 ($4f^6 6s6p$, ${}^9F^o_1$)	10
14,863.85 ($4f^6 6s6p$, ${}^9G^o_1$)	10
16,690.77	2
17,769.67	3
18,225.09	2
18,475.24	1
18,985.75	2
20,091.08	4
21,193.68	1
21,748.46 (unclassified)	2
22,313.61	2
22,914.05 ($4f^6 6s6p$, ${}^7G^o_1$)	2
23,080.51 (unclassified)	3
23,629.97	1
26,281.09	4

Table 2 (Continued)

(b) **Absorption spectrum of samarium in a krypton matrix.**

The number in parentheses immediately following the frequency gives the line width in cm^{-1}. The final number is the estimated relative absorption intensity.

Frequency ($\pm$5 cm^{-1})		
17,670	(80)	8
17,770	(80)	8
17,900	(100)	10
19,760	(20)	10
19,860	(160)	6
20,020	(60)	10
20,070	(20)	8
21,190	(160)	8
21,510	(20)	8
21,600	(40)	10
22,290	(60)	6
22,390	(20)	6
22,450	(15)	8
22,810	(60)	2
22,870	(15)	2
22,910	(15)	2
23,050	(40)	2
23,140	(15)	1
23,290	(15)	8
23,410	(15)	1
26,070	(40)	8
26,220	(40)	8
26,410	(100)	2
26,610	(40)	6
26,830	(80)	6

Table 2 (Continued)

(c) Absorption spectrum of samarium in an argon matrix.

The number in parentheses immediately following the frequency gives the line width in cm^{-1}. The final number is the estimated relative absorption intensity.

Frequency ($\pm$ 5 cm^{-1})			Frequency ($\pm$ 5 cm^{-1})		
14,760	(40)	1	17,640	(20)	3
14,860	(30)	1	17,930	(30)	12
14,890	(30)	1	18,130	(15)	6
15,410	(15)	3	18,290	(15)	5
15,460	(15)	5	18,710	(20)	3
15,480	(15)	4	18,980	(15)	2
15,830	(15)	1	19,190	(40)	3
15,860	(15)	1	19,500	(40)	3
15,900	(15)	4	19,660	(20)	3
16,850	(20)	5	19,860	(20)	12
16,920	(20)	4	20,140	(60)	9
17,000	(60)	2	20,190	(20)	9
17,080	(60)	2	21,073	(4)	2
17,170	(30)	6	21,080	(4)	2
17,360	(60)	4	21,087	(4)	2
17,460	(30)	4	21,420	(40)	8
17,560	(20)	3	21,600	(50)	8

Table 2(c) (Continued)

Frequency			Frequency			
21,710	(40)	8	24,270	(15)	4	
21,990	(20)	10	24,956	(10)	2	Fluorescence
22,070	(40)	8	24,994	(10)	1	
22,380	(15)	5	24,478	(10)	2	
22,440	(15)	5	24,517	(10)	1	
22,560	(40)	10	25,880	(5)	8	
22,740	(40)	7	25,900	(5)	8	
22,900	(15)	4	26,380	(15)	4	
22,990	(60)	9	26,430	(15)	4	
23,170	(15)	3	26,540	(10)	4	
23,330	(150)	10	26,590	(10)	4	
23,568	(4)	10	26,660	(15)	5	
23,579	(4)	10	26,690	(10)	5	
23,590	(4)	10	26,820	(15)	3	
23,870	(15)	10	26,890	(15)	3	

Table 3

Atom	Crystal Data Type	Crystal Data Internuclear Separation	Ref.
Samarium	Rhombohedral	3.604 Å = 6.82 a_0	14
Argon	Face centered cubic	7.09 a_0	15
Krypton	Face centered cubic	7.59 a_0	15

a_0 (Bohr radius) = 0.5292 Å

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